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Report No. IITRI-U6002-83
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

National Aeronautics & Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

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May 1 through September 30, 1969

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IITRI Project U6002

Prepared by

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Huntsville, Alabama 35812

November 17, 1969

IIT RESEARCH INSTITUTE

FOREWORD


This is Report No. IITRI-U6002-83 (Triannual Report) of IITRI Project U6002, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." This report covers the period from May 1 through September 30, 1969. Previous Triannual Reports were issued on October 25, 1963; March 5, 1964; July 20, 1964; December 21, 1964; February 23, 1965; July 20, 1965; November 9, 1965; February 21, 1966; July 11, 1966; November 30, 1966; February 28, 1967; September 22, 1967; January 15, 1968; April 15, 1968; October 25, 1968; January 31, 1969 and July 11, 1969.

Major contributors to the program during this period include Gene A. Zerlaut, Project Leader; Dr. Nicholas Ashford, solid-state studies on zinc orthotitanate; John E. Gilligan, general consultation; Frank Jarke, EPR investigations; George Kimura, vacuum technology and space simulation tests; and Frederick O. Rogers, zinc orthotitanate preparation. The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

Prior to March 15, 1966, this contract was funded under Codes 124-09-05-26-04, 124-09-05-00-14, 933-50-01-00-00 and 908-20-02-01-47.

Respectfully submitted,

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

The general requirement under this contract is the development of thermal-control surface coatings that possess very low but stable ratios of solar absorptance (α_s) to infrared emittance (ϵ_h). Historically, this program has been divided into three major phases: (1) inorganic pigment technology, (2) silicone-photolysis and silicone-paint investigations, and (3) general coatings investigations.

The relative emphasis on each major task has varied during the course of the program according to the urgency of the various problems elucidated by our investigations as well as the availability of both funds and personnel. The major emphasis during the past two years has involved the investigation of new, potentially stable white-pigments -- particularly zinc orthotitanate.

The studies reported here include extensive EPR investigations of variously treated samples of zinc orthotitanate pigments and EPR investigations of the precursor oxides and (zinc metatitanate-containing) zinc orthotitanate. Results of x-ray diffraction investigations are also reported.

In our previous preparatory scheme, zinc orthotitanate (Zn_2TiO_4) was prepared by a solid-state reaction at elevated temperatures in air between ZnO and anatase TiO_2 in the mole ratio (2:1). Although a slight excess of TiO_2 was used in that preparatory mixture, residual ZnO always resulted, which was partially removed by washing with acetic acid. The stoichiometry describing the reaction,



suggests that either residual TiO_2 also remained or that other titanates were also formed in the orthotitanate lattice. Thus, in an attempt to drive the reaction (1) to completion, samples

were prepared in which an excess of ZnO was used. According to work done by Kubo, et al (Ref. 1), at relatively low temperatures (780°C), zinc metatitanate in the presence of ZnO, reacts to form zinc orthotitanate



Thus a large excess of ZnO would insure that any zinc metatitanate formed would react to form zinc orthotitanate and the excess ZnO would also insure complete reaction in (1). This would leave only ZnO which could be easily removed by washing with acetic acid. It will be seen that the presence of excess ZnO is critically important in the final product to provide stability against optical damage.

II. EXPERIMENTAL

A. Materials Preparation

1. TiO_2

Samples of TiO_2 were obtained directly from the manufacturer. DuPont was the supplier of rutile TiO_2 (R-900) and anatase TiO_2 (FF). Rutile TiO_2 was also obtained from Union Carbide (OR-600).

2. Pseudo ZnTiO_3 Sample

An attempt was made to prepare pure ZnTiO_3 by heating rutile TiO_2 and ZnO in the mole ratio of 1:1 for 17 hr at 850°C. As reported by Kubo et. al. (Ref. 1), this reaction is difficult to control and x-ray analysis showed that only a small amount of ZnTiO_3 was formed with the bulk being Zn_2TiO_4 .

3. Zn_2TiO_4 Samples

A batch (B-229) of Zn_2TiO_4 was made by heating ZnO (0.5% in excess) with anatase TiO_2 in the mole ratio 2:1 at 925°C for 18 hr. No attempt was made to extract the excess ZnO with acetic acid.

The samples with the description of treatment and sample numbers were then prepared from this main batch (B-229). They are listed in Table 1.

Table 1	
Zn_2TiO_4 SURFACE TREATMENTS	
Sample Number	Treatment
B-233	B-229 refluxed for 4 hr at 100°C in $\text{K}_2\text{O} \cdot \text{SiO}_2$
B-234	B-229 hot mixed for 30 min with $\text{K}_2\text{O} \cdot \text{SiO}_2$
B-235	B-229 cold ground for 2 hr with $\text{K}_2\text{O} \cdot \text{SiO}_2$
B-241	B-229 cooked for 4 hr at 100°C with 5% solution of NaH_2PO_4
B-226	B-229 hot mixed, paddle stirred with $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$
B-230	B-226 paint; ground in Ps-7, 75% PVC; oven dried at 230°F and retreated with $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$

A schematic of the preparation history is presented in Figure 1.

B. X-Ray Studies

Eight samples were selected for study. They were: anatase TiO_2 (FF), rutile TiO_2 (R-900), pseudo ZnTiO_3 (B-256) and Zn_2TiO_4 (B-229, B-233, 3, 3* and 3**). Specimens 3, 3* and 3** were discussed in the last Triannual Report (Ref. 3). They were exposed for 4 hr to K_α radiation from a copper element employing a nickel filter, $\lambda = 1.541 \text{ \AA}$. The cameras used had a diameter of 114.6 mm, therefore, $2\theta_{\text{deg}} = S/2$, where S is the distance between two corresponding arcs in millimeters.

C. EPR Studies

1. Unirradiated Samples

Eleven samples, anatase TiO_2 (FF), rutile TiO_2 (R-900 and OR-600), pseudo ZnTiO_3 (B-256), and Zn_2TiO_4 (B-229, B-233, B-234, B-235, B-241, B-226 and B-230), were placed in quartz sample

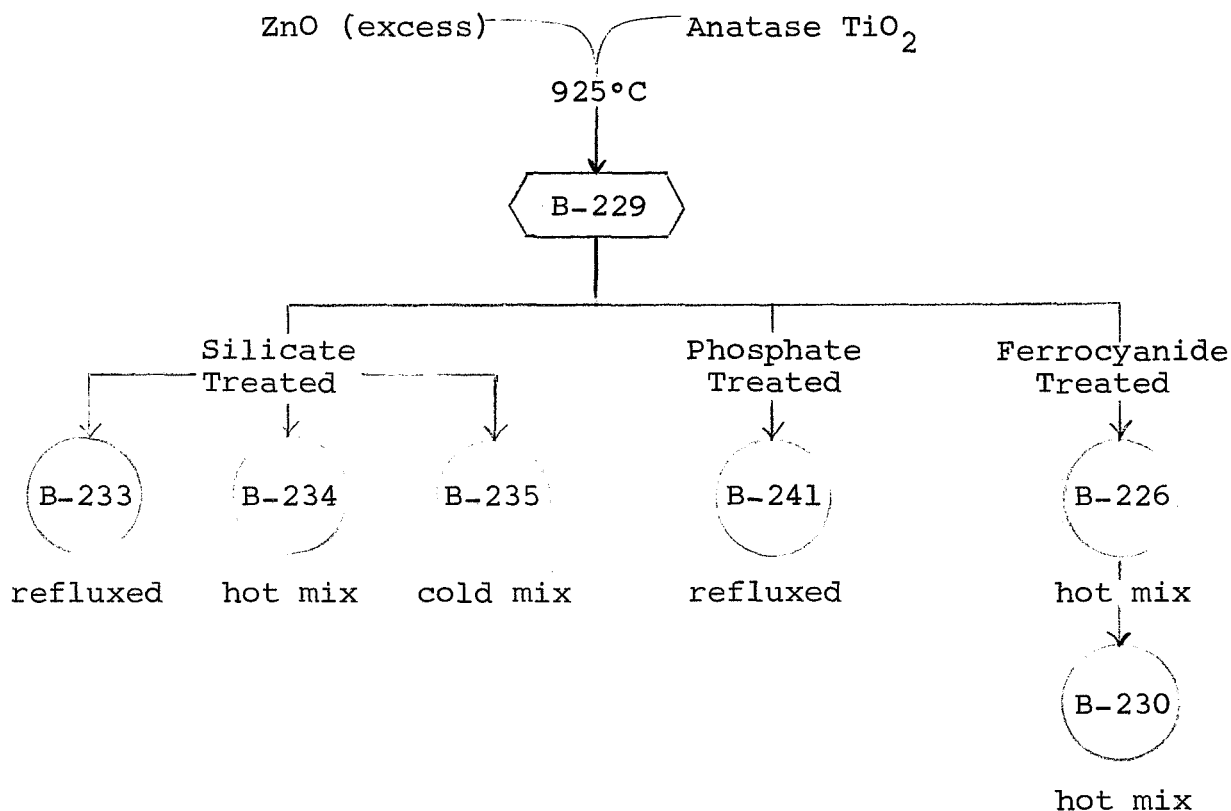


Figure 1: ZINC ORTHOTITANATE SURFACE TREATMENT HISTORY

tubes, outgassed with a mechanical pump, and investigated for EPR absorption at $\sim 77^\circ\text{K}$.

2. Gamma Irradiated Samples

The eleven samples (para. C.1.) were placed in quartz sample tubes, outgassed with a mechanical pump and gamma-irradiated at $\sim 77^\circ\text{K}$ with 5 sources of Co^{60} , totaling 4000 Curies, for 16 hr. The samples were investigated and stored in liquid nitrogen.

3. Optically Irradiated Samples

Five samples, anatase TiO_2 (FF), pseudo ZnTiO_3 (B-256) and Zn_2TiO_4 (B-229, B-233 and B-241) were placed in the irradiation apparatus described previously (Ref. 2), evacuated to 1×10^{-7} Torr, and outgassed at $\sim 120^\circ\text{C}$ under high vacuum for 16 hr. The samples were irradiated at 6 solar equivalents for 24 hr (employing an AH-6 source). It was inferred from the results of the anatase

experiment that the temperature of the sample must remain below 600°C, the temperature of conversion of anatase TiO_2 to rutile TiO_2 . The procedure employed was: one minute before the irradiation is terminated, a stream of nitrogen gas ($\sim 100^\circ\text{K}$) is directed against the EPR tube containing the sample. After the termination of irradiation, the evacuated sample is sealed off while the vacuum is maintained at 1×10^{-7} torr and quickly cooled to $\sim 77^\circ\text{K}$. The samples were examined at $\sim 77^\circ\text{K}$ for EPR absorption within an hour after the termination of irradiation.

III. RESULTS

A. X-Ray Studies

1. Samples 3, 3* and 3**

Examination of the x-ray data in Figure 2 for the zinc orthotitanate samples previously investigated by optical reflectance studies and by EPR (Ref.'s 2, 3) shows that while 3 and 3* do not exhibit patterns for ZnO , TiO_2 or ZnTiO_3 , sample 3** indicates the presence of ZnO and rutile TiO_2 . No ZnTiO_3 was indicated in sample 3**.

2. Pseudo ZnTiO_3 (B-256)

The x-ray data indicate that while ZnTiO_3 is present in this sample, most of the sample is in fact Zn_2TiO_4 with some rutile TiO_2 . No ZnO was indicated.

3. Control Sample B-229

The x-ray data indicate that aside from the bulk Zn_2TiO_4 , ZnO is also present. No TiO_2 was indicated.

4. Silicate Treated B-233

The x-ray data indicate that aside from the bulk Zn_2TiO_4 , ZnO is also present. No TiO_2 was indicated.

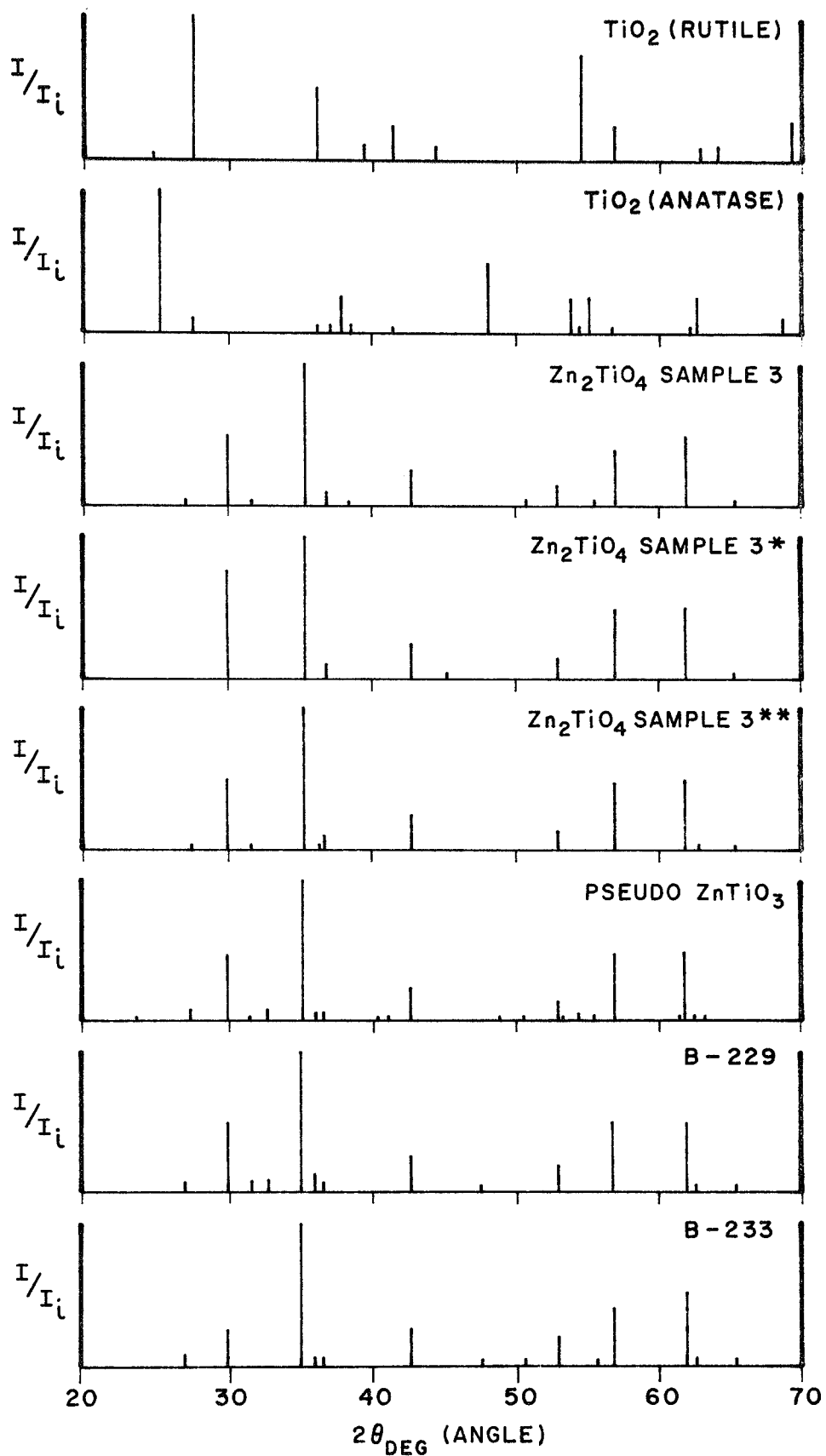


Figure 2: GRAPHICAL REPRESENTATION OF RESULTS OF X-RAY DIFFRACTION STUDY

The x-ray data also indicated that FF anatase TiO_2 contains rutile and that, as expected, the rutile samples contain no anatase. Small amounts of unidentified impurities are also indicated by the x-ray data, whose presence cannot be correlated with the optical or EPR results, and which are thought to be unimportant. It should be noted that where x-ray studies do not indicate the presence of ZnO or TiO_2 , some may be present in small quantities nonetheless, and may be detected by the more sensitive optical or EPR investigations.

B. EPR Studies

1. Unirradiated Samples

The resonance "n" described in the previous report (Ref. 3) turns out to be a contaminant in the EPR cavity and not a property of the samples at all.

No EPR was observed in the rutile TiO_2 and the EPR spectra of anatase TiO_2 are shown in Figure 3. No EPR was observed in the psuedo ZnTiO_3 (B-256).

The control zinc orthotitanate sample B-229 contains only the sharp (~ 2 gauss) resonance "y", shown in Figure 4, with g-values listed in Table 2. The remaining zinc orthotitanate samples, all derived from the precursor B-229 (silicate treated, phosphate treated and ferro-cyanide doped), all exhibited the same resonance "y", with essentially the same g-values (Table 2).

2. Gamma-Irradiated Samples

The TiO_2 , both rutile and anatase, exhibited essentially the same spectra. The g-values are listed in Table 3 and the EPR spectra found in rutile TiO_2 (sample R-900) are shown in Figure 5. The resonances "a" and "b" are definitely found, while resonances which might be "c", "d" and "e" are possibly present. The resonances "k", "x" and "y" are not found.

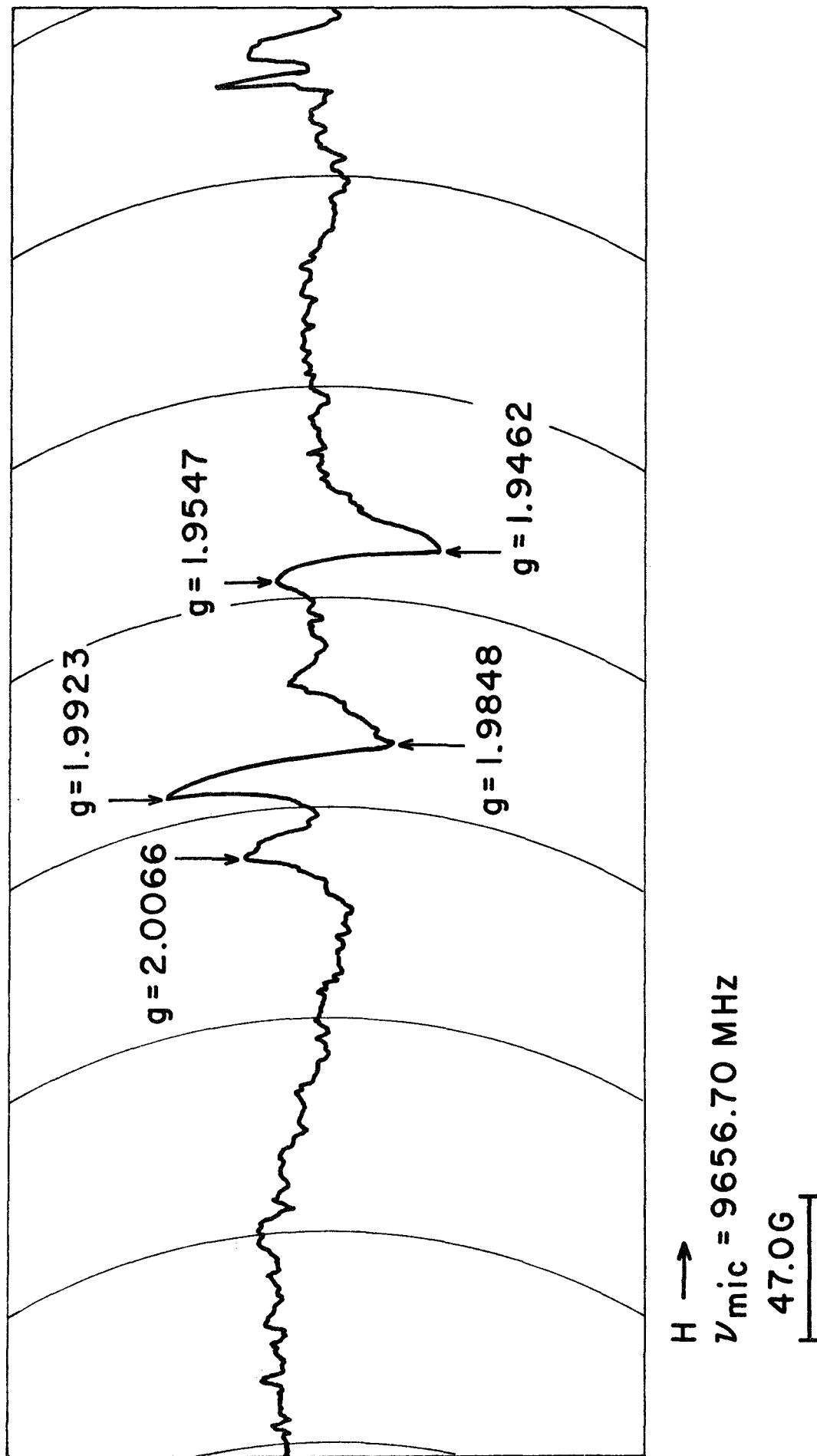
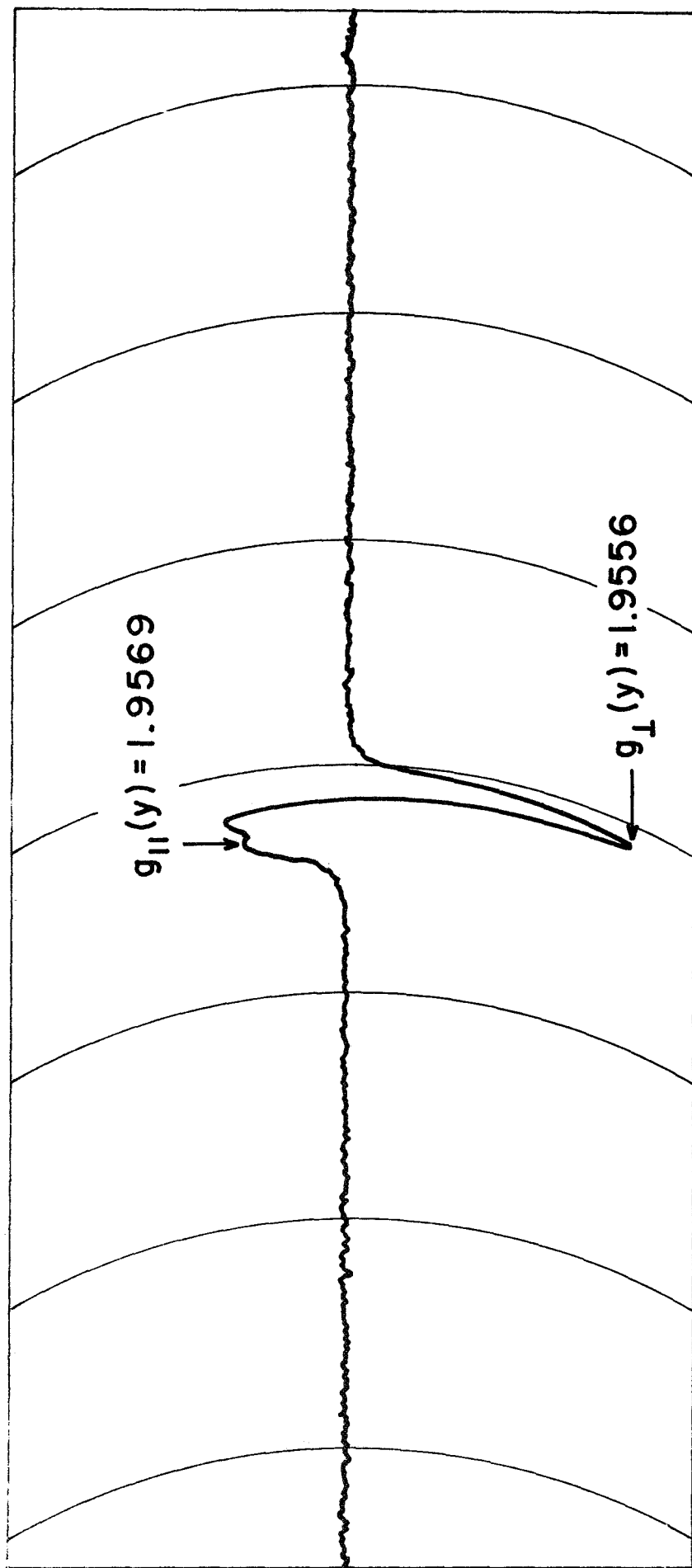


Figure 3: EPR AT $\sim 77^\circ\text{K}$ OF UNIRRADIATED ANATASE TiO_2 , SAMPLE FF, MODULATION - 8.21G



H →

$\nu_{\text{mic}} = 9655.25 \text{ MHz}$

6.7G



Figure 4: EPR AT $\sim 77^\circ\text{K}$ OF UNIRRADIATED Zn_2TiO_4 , SAMPLE B-229, MODULATION - 0.83G

Table II

MAGNETIC RESONANCE IN UNIRRADIATED SAMPLES (g-VALUES)

<u>Value</u>	<u>Zn₂TiO₄ (B-229)</u>	<u>Zn₂TiO₄ (B-233)</u>	<u>Zn₂TiO₄ (B-234)</u>	<u>Zn₂TiO₄ (B-235)</u>	<u>Zn₂TiO₄ (B-241)</u>	<u>Zn₂TiO₄ (B-226)</u>	<u>Zn₂TiO₄ (B-230)</u>	<u>Lit. Values</u>
g_{II} (Y)	1.9570	1.9569	1.9569	1.9569	1.9570	1.9568	1.9569	1.957 (Ref.)
g_I (Y)	1.9556	1.9556	1.9556	1.9555	1.9556	1.9556	1.9556	1.956 (Ref.)

Table III

MAGNETIC RESONANCES IN γ -IRRADIATED SAMPLES

Value	TiO ₂ Anatase (F.F.)	TiO ₂ Rutile (R-900)	TiO ₂ Rutile (OR-600)	Pseudo ZnTiO ₃ (B-256)	B-229	B-233	B-234	B-235	B-241	B-226	B-230
$g(k)$	---	---	---	2.0136	2.0130	2.0129	2.0129	2.0129	2.0129	2.0132	2.0125
$g_I(c)$	2.0107	2.0105	2.0105	2.0095	2.0104	2.0110	2.0106	2.0106	2.0104	2.0100	2.0107
$g_{II}(e)$	---	---	---	2.0060	2.0065	2.0066	2.0065	2.0064	2.0065	2.0067	2.0067
$g_{II}(d)$	---	---	---	2.0048	2.0052	2.0053	2.0052	2.0050	2.0050	2.0055	2.0046
$g_I(d)$	---	---	---	2.0039	2.0040	2.0040	2.0039	2.0039	2.0040	2.0041	2.0040
$g_{II}(c)$	2.0030	2.0029	2.0030	2.0026	2.0027	2.0032	2.0029	2.0029	2.0030	2.0028	2.0031
$g(b)$	2.0015	2.0015	2.0015	2.0015	2.0015	2.0014	2.0015	2.0014	2.0015	---	2.0014
$g(a)$	2.0005	2.0005	2.0006	2.0005	2.0006	2.0006	2.0005	2.0004	2.0005	2.0005	2.0006
$g_I(x)$	---	---	---	1.9785	1.9781	1.9787	1.9787	1.9785	1.9787	---	1.9699
$g_{II}(y)^*$	---	---	---	---	1.9567	1.9567	1.9568	1.9567	1.9569	1.9570	1.9569
$g_I(y)^*$	---	---	---	---	1.9554	1.9555	1.9555	1.9554	1.9555	1.9554	1.9556

*Literature values are: $g_{II}(y) = 1.957$, $g_I(y) = 1.956$, see Ref. 4.

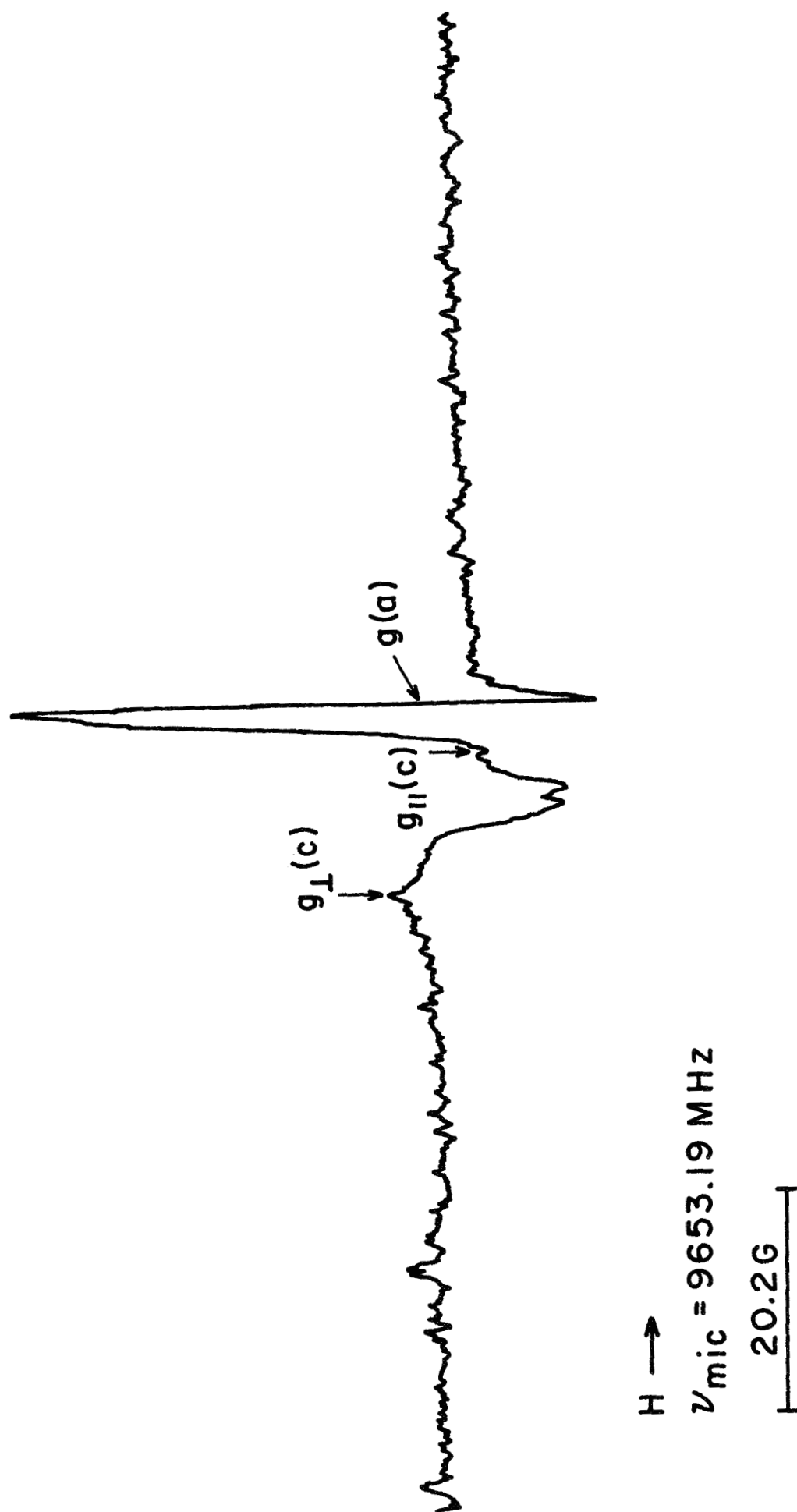


Figure 5: EPR AT $\sim 77^{\circ}\text{K}$ OF GAMMA-IRRADIATED RUTILE TiO_2 , SAMPLE R-900, MODULATION - 0.52G

In pseudo ZnTiO_3 (B-256), the resonances "a", "b", "c", "d", and "e" are clearly indicated (Figure 6 and Table 3) as well as "k" and "x". The resonance "y" is not found.

The EPR spectra found in the control sample B-229 are shown in Figure 7 with g-values listed in Table 3. Resonances "a", "b", "c", "d", "e", "k", "x" and "y" are all present. While some differences in intensity are apparent in all the derivative samples, all the resonances present in the B-229 are present in the derivative samples (Figures 8, 9 and 10, Table 3).

3. Optically-Irradiated Samples

The control zinc orthotitanate sample B-229 exhibited only the sharp resonance "y" also found in the unirradiated material (Figure 11, Table 4). The silicate treated sample B-233 (Figure 12, Table 4), and the phosphate treated sample B-241 (Figure 13, Table 4) exhibited the same resonance "y".

The pseudo ZnTiO_3 (B-256) exhibits the resonance "x", and "y" to a much smaller extent than found in the orthotitanate-prepared samples (Figure 14, Table 4).

Optically irradiated anatase TiO_2 (FF) exhibits the same spectra as the unirradiated material (Figure 15). This anatase contains some rutile and the resonance "x" is not observed in the optically irradiated material.

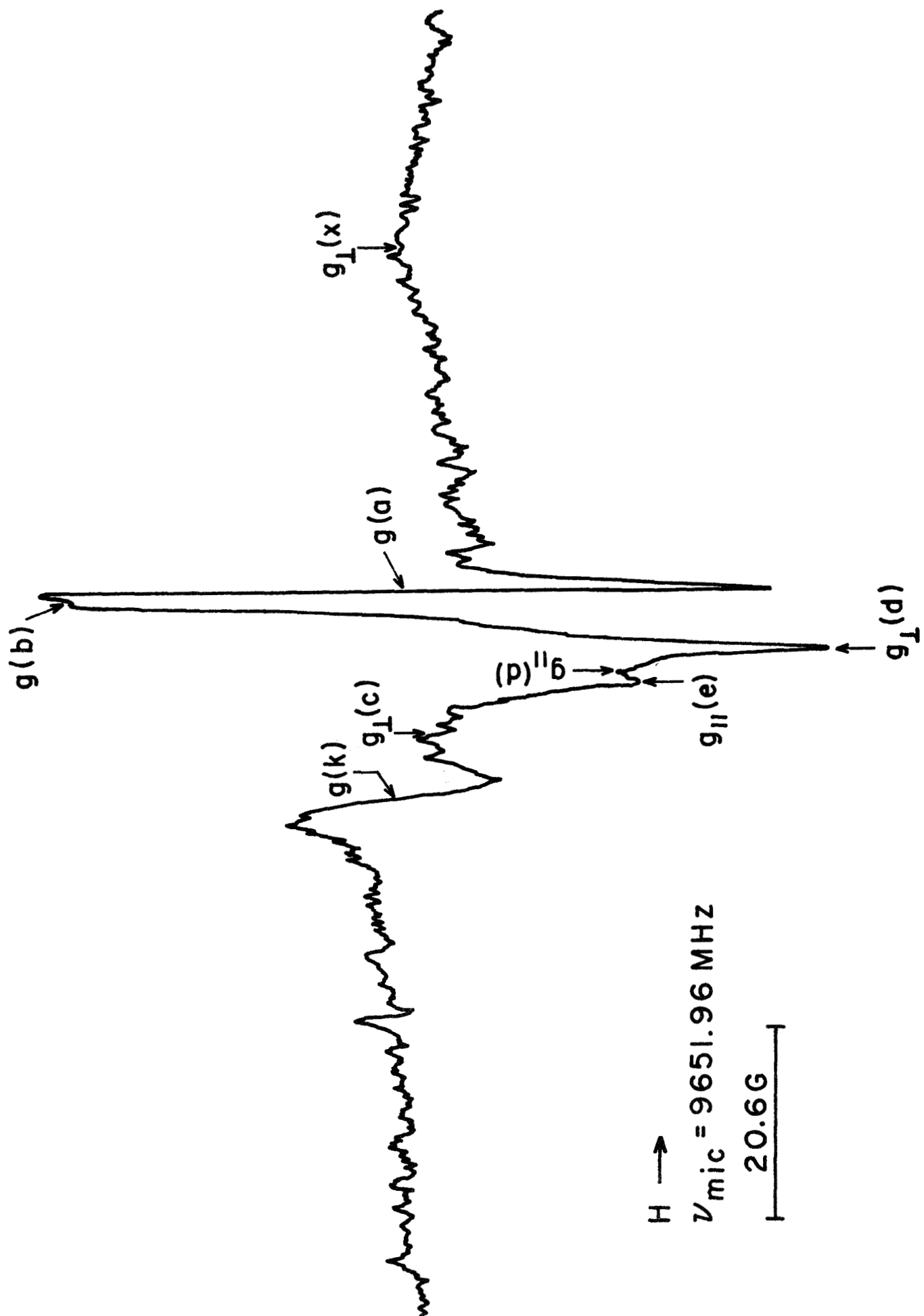


Figure 6: EPR AT $\sim 77^\circ\text{K}$ OF GAMMA-IRRADIATED PSEUDO ZnTiO_3 , SAMPLE B-256, MODULATION - 0.52G

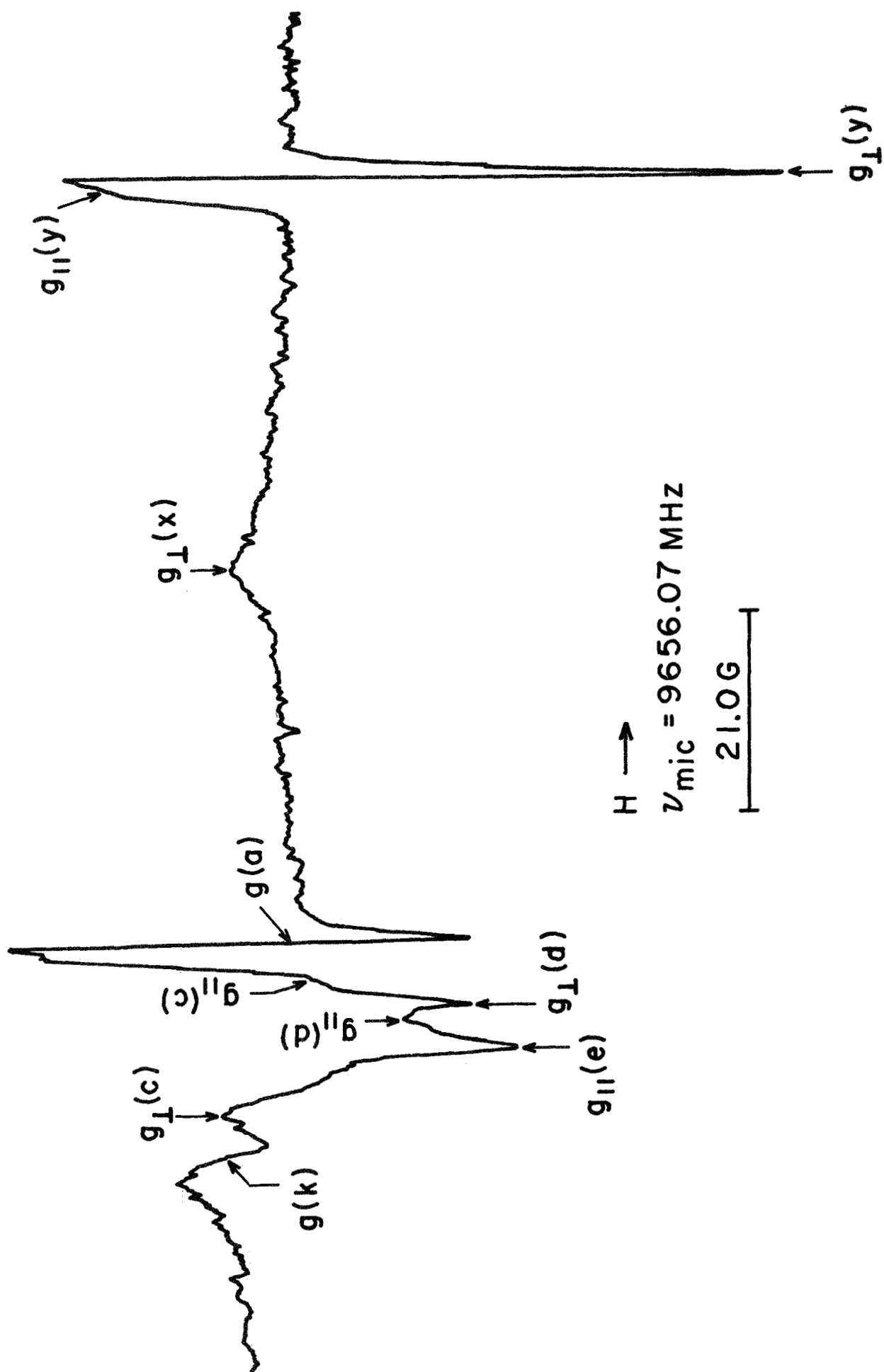


Figure 7: EPR AT $\sim 77^\circ\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-229, MODULATION - 0.52G

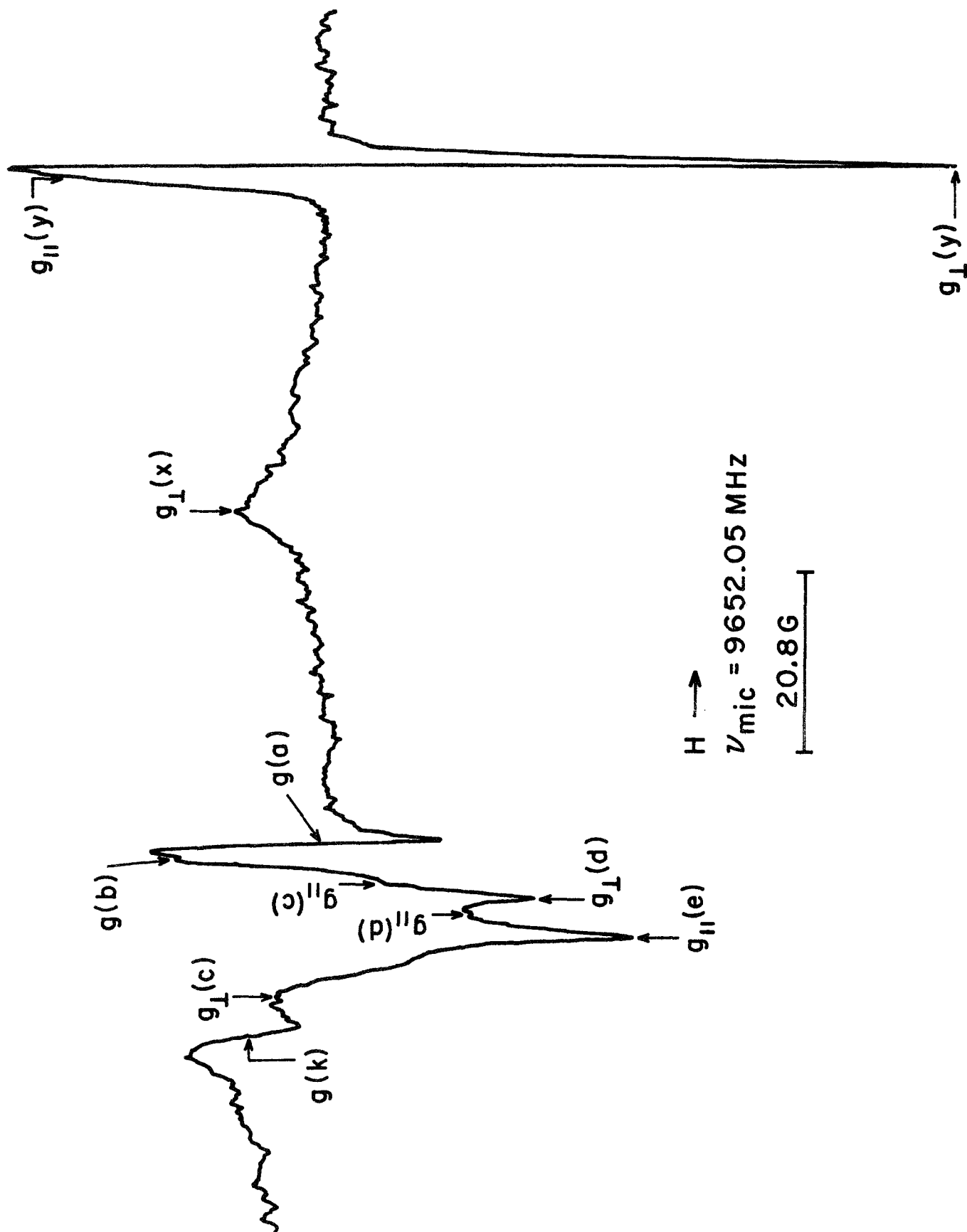


Figure 8: EPR AT $\sim 77^\circ\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-233, MODULATION - 0.52G

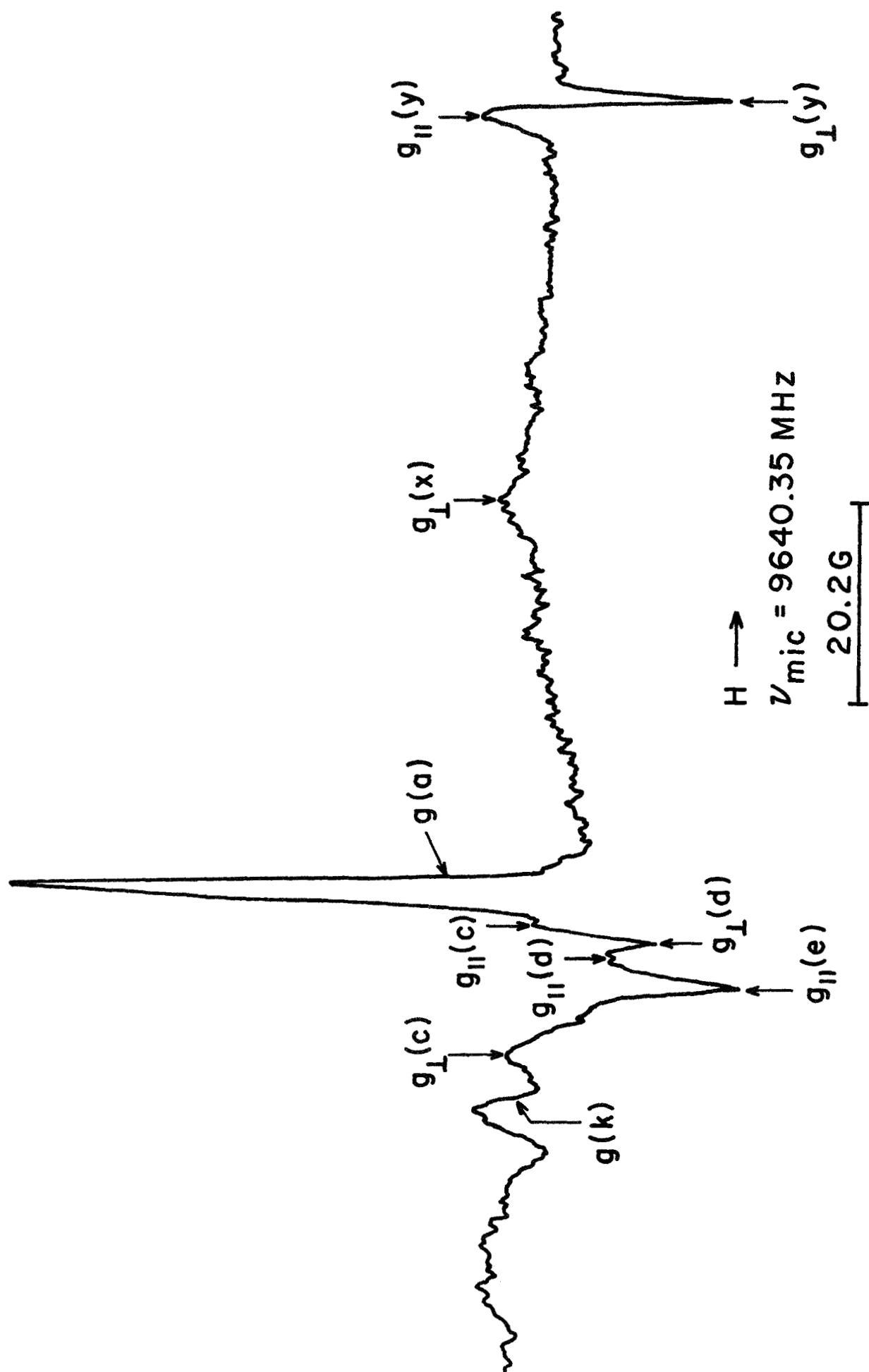


Figure 9: EPR AT $\sim 77^\circ\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-241, MODULATION - 0.52G

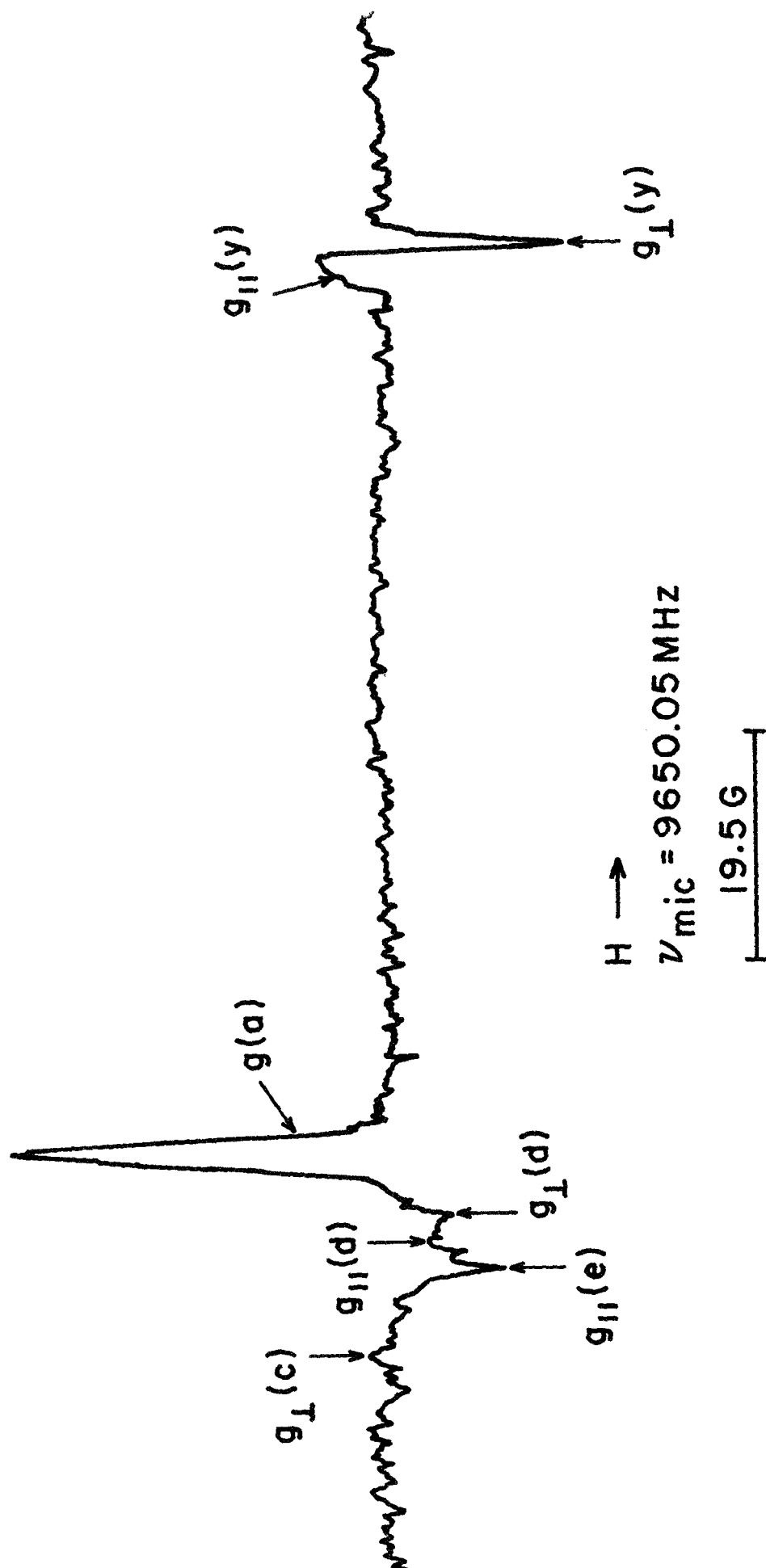


Figure 10: EPR AT $\sim 77^{\circ}\text{K}$ OF GAMMA-IRRADIATED Zn_2TiO_4 , SAMPLE B-226, MODULATION - 0.52G

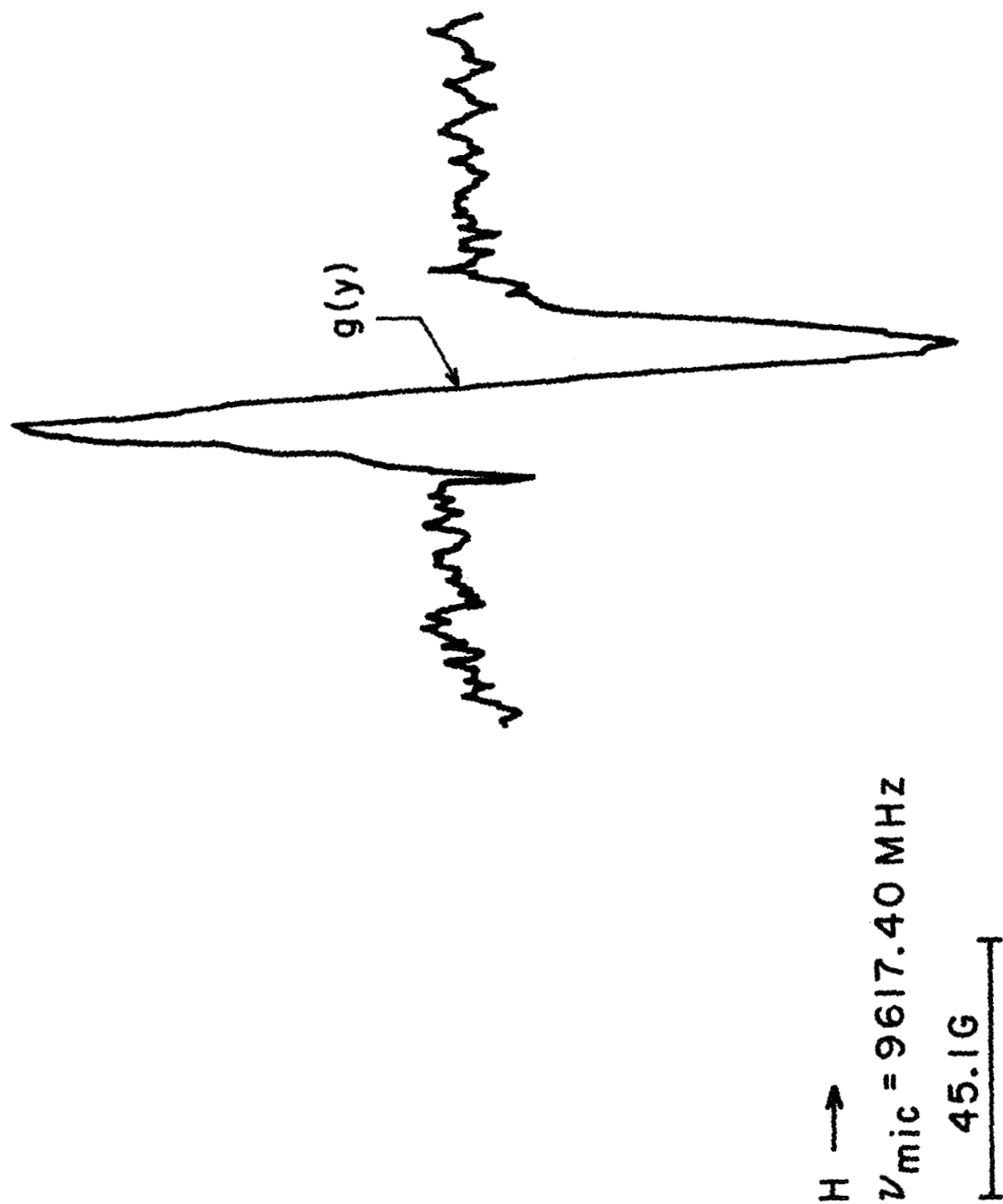


Figure 11: EPR AT $\sim 77^\circ\text{K}$ OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-229, MODULATION - 11.88G

Table IV

MAGNETIC RESONANCE IN OPTICALLY IRRADIATED SAMPLES (g-VALUES)

<u>Value</u>	<u>TiO₂ Anatase (F.F.)</u>	<u>Pseudo ZnTiO₃ (B-256)</u>	<u>B-229</u>		<u>B-233</u>		<u>B-241</u>		<u>Literature Values</u>
$g_I(x)$	---	1.9762	---		---		---		
$g_{II}(y)$	---	1.9563	1.9567		1.9564		1.9567		1.957 (Ref. 4)
$g_I(y)$	---	1.9553	1.9553		1.9552		1.9551		1.956 (Ref. 4)

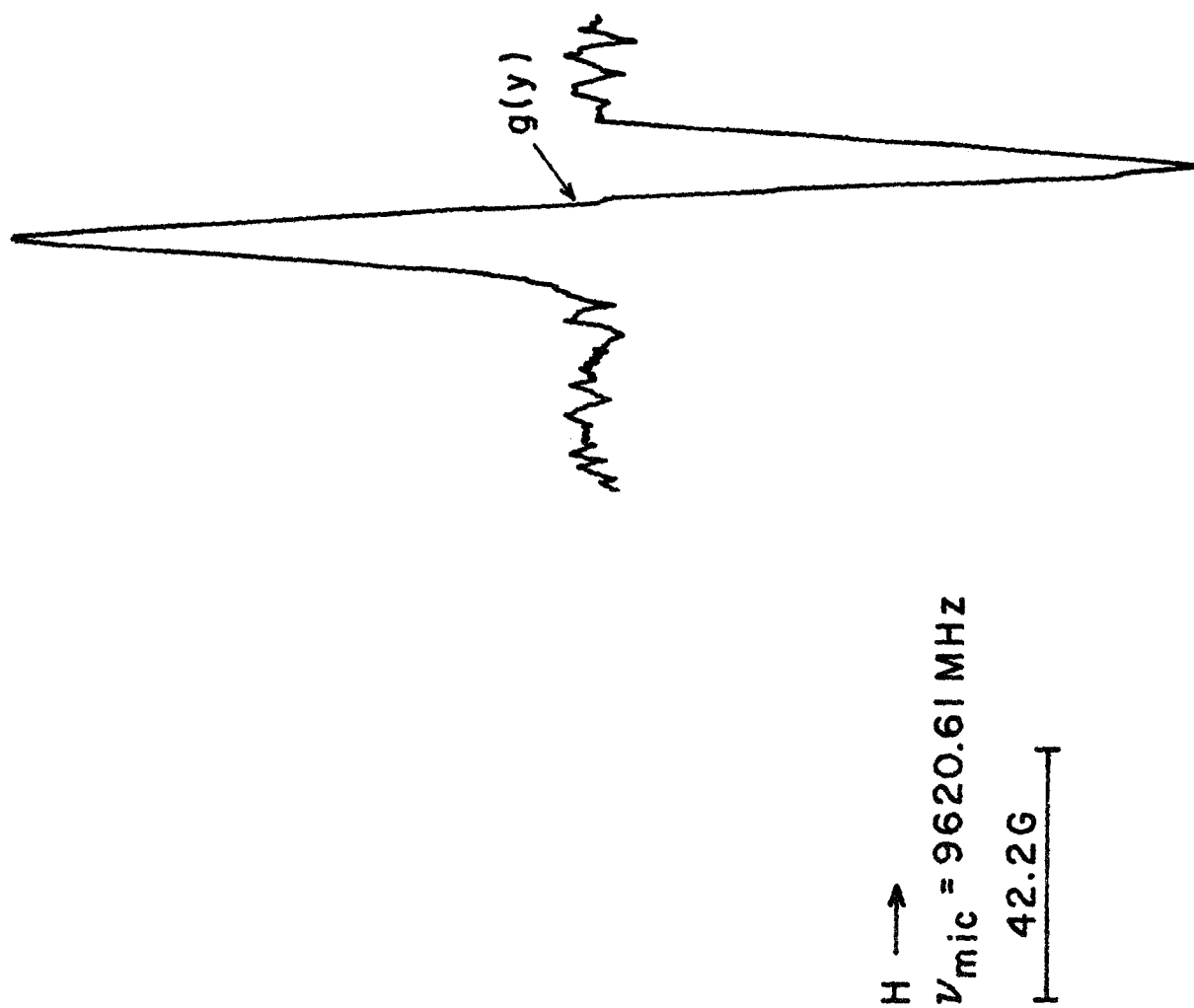


Figure 12a: EPR AT $\sim 77^\circ\text{K}$ OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-233, MODULATION - 11.88G

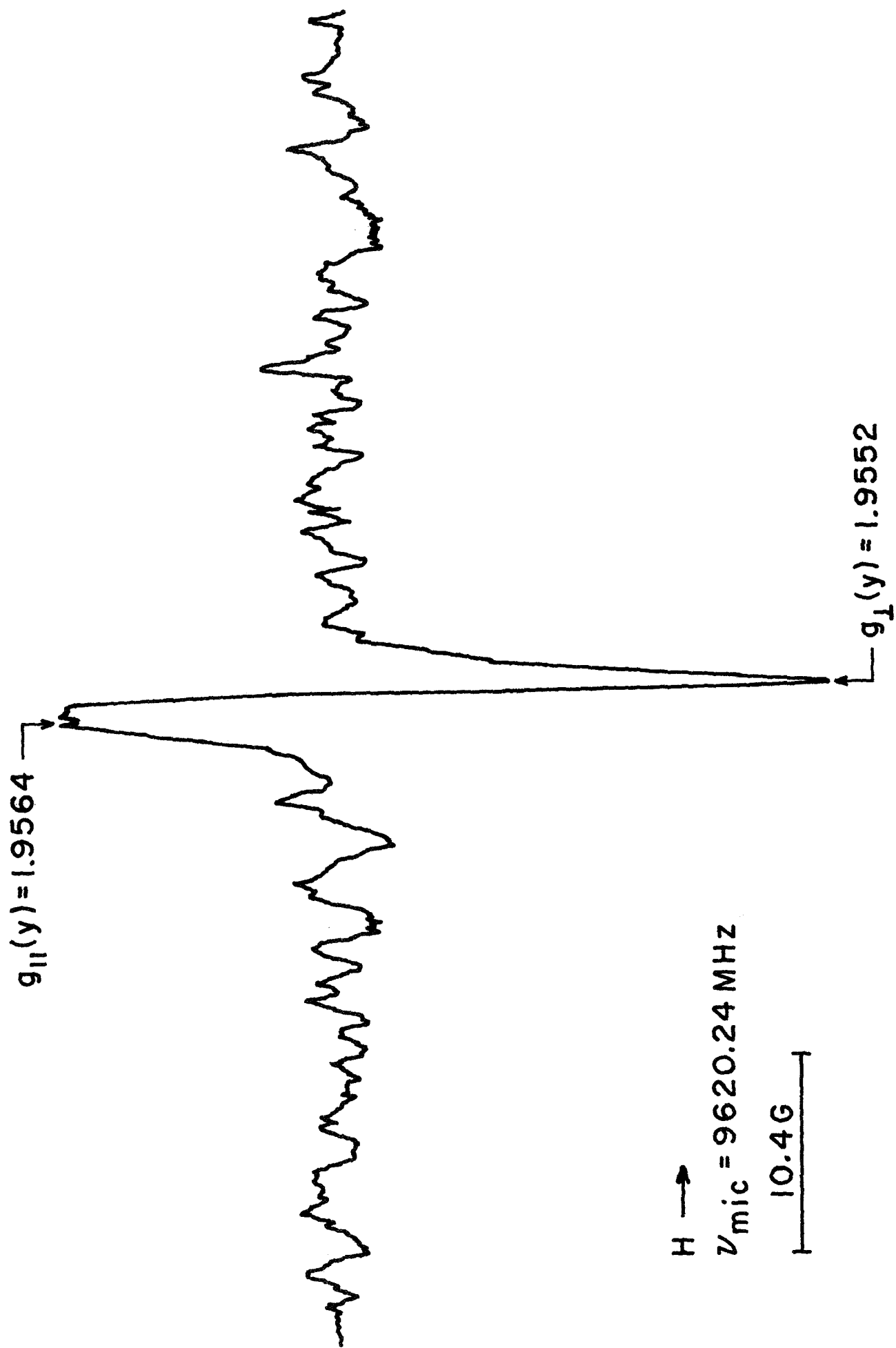


Figure 12b: EPR AT $\sim 77^\circ \text{K}$ OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-233, MODULATION $\sim 0.34 \text{G}$

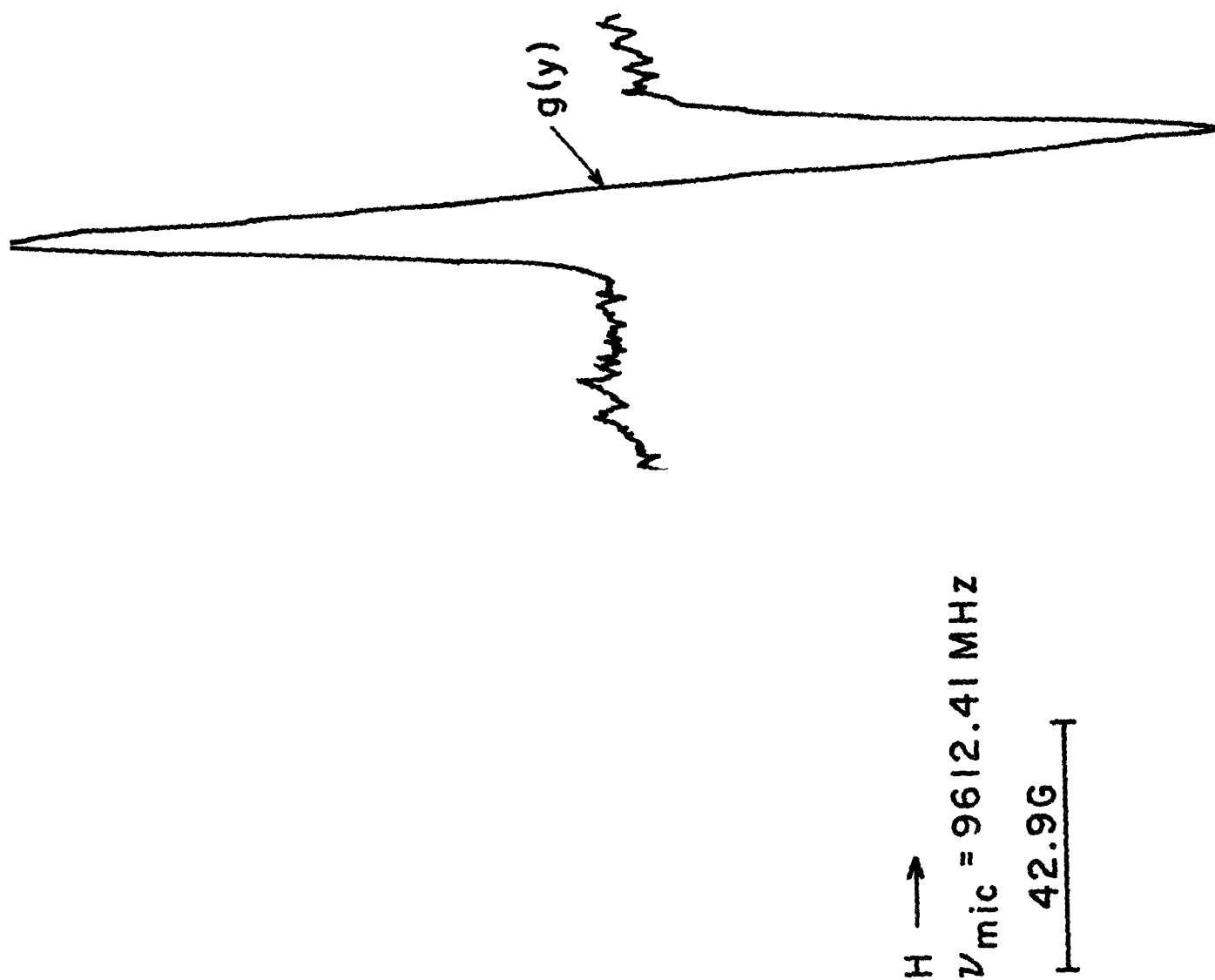


Figure 13: EPR AT $\sim 77^\circ K$ OF OPTICALLY IRRADIATED Zn_2TiO_4 , SAMPLE B-241, MODULATION $\sim 11.88G$

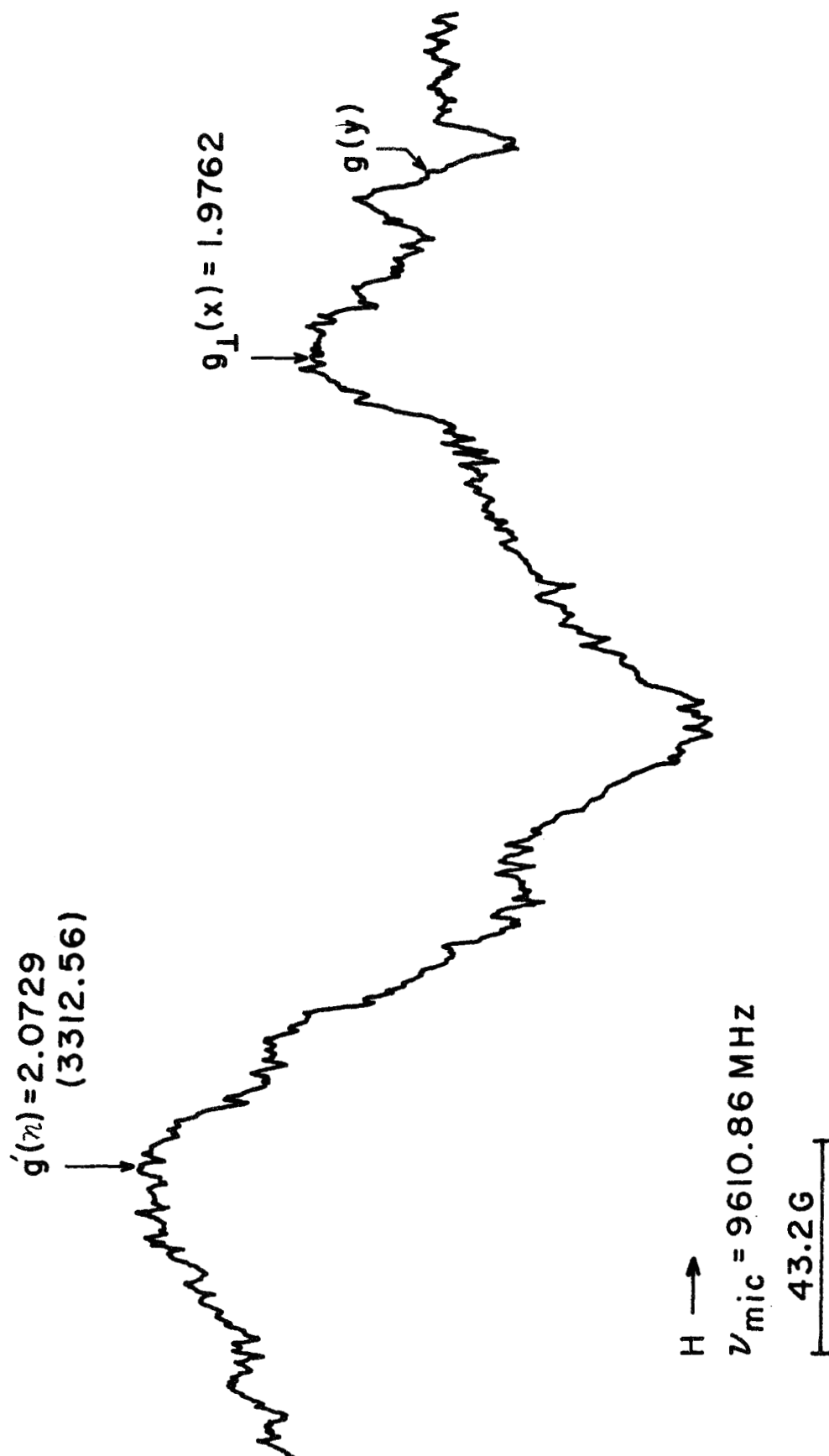


Figure 14: EPR AT $\sim 77^\circ\text{K}$ OF OPTICALLY IRRADIATED PSEUDO ZnTiO_3 , SAMPLE B-256, MODULATION - 11.88G

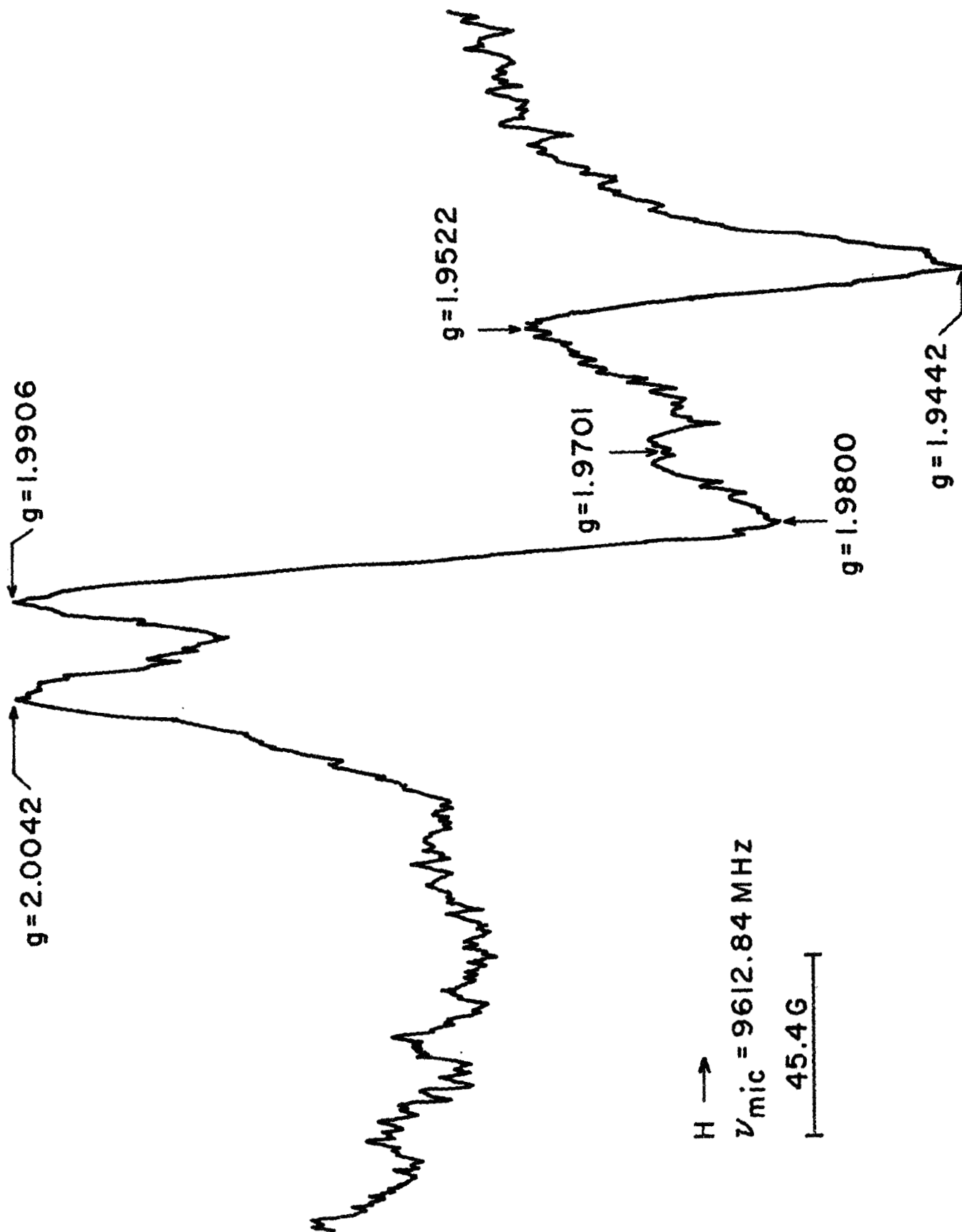


Figure 15: EPR AT $\sim 77^\circ\text{K}$ OF OPTICALLY IRRADIATED ANATASE TiO_2 , SAMPLE FF, MODULATION - 11.88G

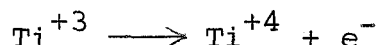
IV. CORRELATION OF THE OPTICAL REFLECTANCE, EPR AND X-RAY STUDIES AND CONCLUSIONS

A. The Resonance "y"

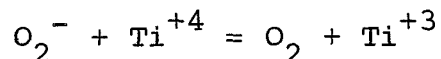
Resonance "y" with $g_1 = 1.9555$ and $g_{11} = 1.9568$ with an error of ± 0.0001 is identified as the same resonance observed in ZnO heat treated at 900°C in air by Kasai (Ref. 4) and attributed to conduction electrons in ZnO by Sancier (Ref. 5).

B. The Resonance "x"

Resonance "x" is thought to be Ti^{+3} in rutile TiO_2 present in orthotitanate material which can absorb radiation at $\sim 0.9\mu$ to undergo (reversible) ionization



The center "x" seems identical with a center called "c" by Chester (Ref. 6) found in single crystal rutile heated at elevated temperatures ($625 - 1100^\circ\text{C}$) in air with $g_1 = 1.976$ and $g_{11} = 1.941$ and axial symmetry about the crystalline "c" axis, and by Kiselev and Uvarov (Ref. 7) in polycrystalline TiO_2 , calcined in air at 450°C for 30 min with precisely the same g-values and general shape. The evidence strongly suggests that Ti^{+3} is the center "x" observed by us and in the references cited. The Ti^{+3} can originally be created by photodesorption of oxygen on the surface of the material according to

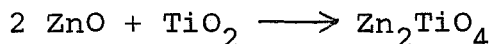


or by a similar thermal process at very high temperatures as realized during plasma annealing (as at a ΔT of 2900°C , see Ref. 3).

C. Zinc Orthotitanate

Zinc orthotitanate materials prepared prior to and including the samples 1, 2, 3, 4, 5 and 6 (see Table 2, Ref. 3) were prepared using a slight excess of TiO_2 . The resonance "y" was

never observed in any of these materials, irradiated or unirradiated (prior to plasma-annealing). This is to be expected if the reaction



went as far as it could go, using up all the ZnO present. The resonance "x" was observed in all these materials when irradiated with ultraviolet. The excess TiO_2 was detected by EPR techniques on gamma-irradiated material (see EPR of gamma-irradiated TiO_2 , Figure 5), even though, in the case of sample 3, x-ray studies did not reveal any TiO_2 .

D. The Sample B-229 - Pseudo ZnTiO_3

An attempt to make pure ZnTiO_3 , starting with equimolar quantities of the precursor oxides, was not successful (probably because too high a firing temperature was inadvertantly achieved). Mostly Zn_2TiO_4 was formed, with some ZnTiO_3 and TiO_2 . The facts that a much smaller amount of the resonance "y" was detected by EPR (hence very little ZnO was present, as expected) and the resonance "x" was present in optically irradiated material give support to the thesis that ZnO prevents the creation of the center "x" by ultraviolet irradiation in vacuum. The center "x" is now most certainly established to be in the rutile TiO_2 material, and may not be in the metatitanate (since it is observed where x-ray analysis does not indicate the presence of metatitanate, such as in samples 3, 3* and 3** and in orthotitanate materials prepared prior to these samples). Also, the center displays the g-values for Ti^{+3} found in rutile TiO_2 material (Ref.'s 6, 7). The fact that "x" is observed in optically irradiated anatase with rutile TiO_2 (FF), is not surprising since that material has not been heated (as were the orthotitanate materials). (The confirming EPR and reflectance investigations of optically irradiated rutile TiO_2 which has been heated in air and ZnTiO_3 ought to be done for completeness.)

E. The Samples 3, 3*, 3** and Plasma-Annealing (Ref. 3)

The facts that sample 3 (a) does not contain a detectable amount of ZnO by x-ray techniques, (b) that large optical damage is observed at $\sim 0.9\mu$ shown in the reflectance spectra of the previous report (Figure 14, Ref. 3), and (c) that the resonance "x" is observed, are understandable in the light of our thesis that ZnO must be present to prevent the creation of damage by the center "x". Low temperature plasma-annealing resulting in sample 3* creates the center "x" thermally without ultraviolet irradiation, as with rutile heated in air (Ref.'s 6, 7), and also results in a small amount of ZnO by decomposition which prevents the center "x" from causing optical damage. The higher plasma-annealed sample 3** results in the thermal creation of "x" as well and a great deal of optical damage in the infrared, due to the presence of a great quantity of ZnO caused by decomposition and confirmed by the x-ray studies; but severe damage at $\sim 0.9\mu$ is not observed. The resonance "y" is not observed in 3** probably because of the high temperature to which the material was subjected in plasma-annealing.

F. Zn_2TiO_4 Prepared with Excess ZnO

The control sample B-229, as well as the derivative samples all display the ZnO resonance "y" in unirradiated and gamma or ultraviolet irradiated material. The resonance "x" is not observed in these materials when ultraviolet irradiated. Thus not only does ZnO prevent damage by the optical absorption at $\sim 0.9\mu$ of the center "x", but it prevents the creation of the center "x" altogether by ultraviolet radiation. Only if high temperatures are achieved, as in plasma-annealing, will ZnO be coexistent with the center "x".

The silicate and phosphate treatments probably prevent even small (undetected) amounts of "x" from forming, by replacing O_2^- on the surface with the silicating or phosphating species.

G. Conclusions

An excess of ZnO in the preparative scheme for the production of Zn_2TiO_4 produces not only an essentially complete reaction, but is necessary to prevent the ultraviolet creation of Ti^{+3} in the rutile TiO_2 impurity in the orthotitanate material and the ultraviolet damage of Ti^{+3} if it happens to be present at all, created by thermal means. Zinc oxide in small amounts appears to stabilize zinc orthotitanate from optical damage. That this is in fact a real effect due to ZnO itself, or a manifestation of excess zinc oxide, insuring a more complete reaction, has not been unequivocally determined. The fact that sample 3**, containing enough ZnO and TiO_2 to be detected by x-ray investigation, does not display severe optical damage although "x" is present indicates that the ZnO directly prevents damage at $\sim 0.9\mu$.

Plasma annealing at too high a temperature can be harmful in that it can create (thermally) Ti^{+3} , but, if the temperature is optimized, can result in optically stable material in that the protective ZnO can be created by decomposition in just small enough amounts not to be responsible for the optical damage itself.

References

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